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EPR investigation of manganese ions in B_2O_3·BaO glass matrix

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Glasses of the xMnO·(100-x)[$3B_2O_3$·BaO] system, with 0.5≤x≤50 mol% were prepared and investigated by EPR measurements. Information concerning the structural details of the vitreous matrix revealed by Mn^{2+} paramagnetic ions distribution on different structural units building the network and coordination were obtained. EPR absorption spectra due to Mn^{2+} ions were detected for all the investigated samples. The distribution of the Mn^{2+} ions on several structural units of vitreous matrix revealed by EPR spectra structure depends on the MnO content. In the low concentration range isolated Mn^{2+} ions were identified in sites of slightly tetragonally distorted octahedral symmetry. They give rise the absorption centered at g_{eff} ≈2.0 showing a resolved hyperfine structure up to 5 mol% MnO. There are also isolated Mn^{2+} ions in sites of heavily distorted octahedral symmetry but with strong crystalline fields giving rise to absorption at g_{eff} ≈4.3. Their intensity is small enough comparatively with those centered at g_{eff} ≈ 2.0 indicated a relatively low concentration of Mn^{2+} ions involved in such structural units. In the high concentration range, 10 ≤ x ≤ 50 mol% the progressive clustering of Mn^{2+} ions was evidenced by the evolution of the corresponding absorption line at g_{eff} ≈2.0. Its line-width depends on concentration showing a dipolar broadening within 0.5 ≤ x ≤ 10 mol% and superexchange narrowing for x ≥ 10 mol%.

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1. Introduction

Manganese ions have been very frequently used as paramagnetic probes for exploring the structure and the properties of vitreous systems. The EPR is very sensitive to changes in paramagnetic ions vicinity and may offer valuable information about the structural units evolution, the strengths of bonding, the valence state and the distribution mode of the manganese ions in the network of oxide glasses [1-7].

Glasses such as borate [5- 8], silicate [9-11], phosphate [11], tellurite [12, 13], bismuthate [14, 15], chalcogenide [16, 17] and halide [18, 19] doped with manganese were investigated by means of Mn^{2+} ions EPR spectroscopy. Generally, the absorption spectra consist of resonance lines centered at g_{eff} ≈ 2.0, g_{eff} ≈ 4.3 and g_{eff} ≈ 3.3 values. The g_{eff} ≈ 2.0 was generally attributed to isolated paramagnetic centers in octahedral symmetric sites slightly tetragonally distorted, or to exchange-coupled pair ions [5]. There are also strongly distorted sites of isolated Mn^{2+} ions in octahedral vicinities subjected to strong crystalline field effects, given rise to absorption at g_{eff} ≈4.3 and g_{eff} ≈3.3 values [10, 18].

Our results, obtained by means of EPR measurements, concerning the structural details of the $3B_2O_3$·BaO vitreous matrix revealing the Mn^{2+} ions distribution on various structural units and also the interactions involving them are presented in this paper.

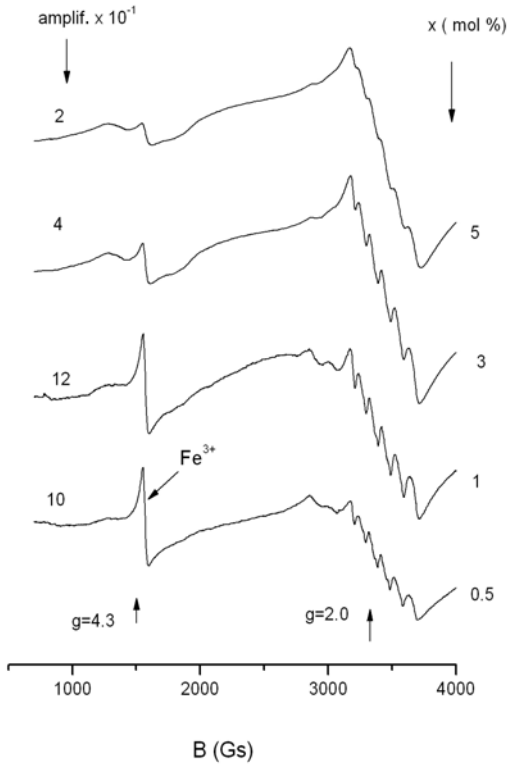
2. Experimental

Glasses of the x MnO·(100-x)[$3B_2O_3$·BaO] system were prepared using reagent grade purity of $MnCO_3$, H_3BO_3 and $BaCO_3$. The mixtures mechanically homogenized were melting in sintered corundum crucibles at 1250 ^oC for 30 minutes. The mixtures were put into the electrical furnace directly at this temperature. By X-Ray diffraction, no crystalline phases were revealed up to 50 mol % MnO.

The EPR measurements were recorded at room temperature in X band frequency (9.4 GHz) and 100 KHz field modulations with an ADANI Portable EPR PS 8400 type spectrometer. The same quantities of powdered samples were studied in fused tubular holders of the same caliber.

3. Results and discussion

The detected spectra for all the samples are presented in Fig. 1 and are typical for the Mn^{2+} ($3d^5$, $^6S_{5/2}$) ions in vitreous system [4,5, 19 -24]. The EPR spectra for the glasses with x < 10 mol% exhibit two main resonance signals, at g_{eff} ≈ 2.0 and g_{eff} ≈4.3 values, their relative intensity depending on the manganese content. The spectral structure corresponding to higher MnO content in the glass matrix reduces to a single absorption line at g_{eff} ≈ 2.0.



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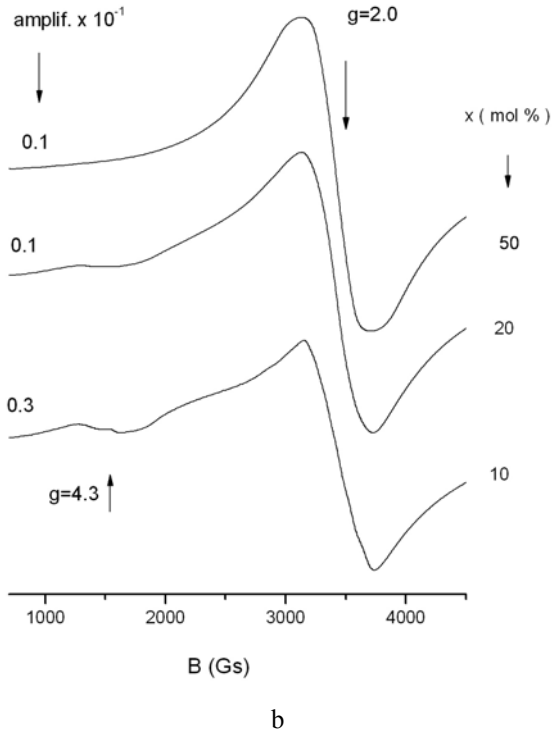

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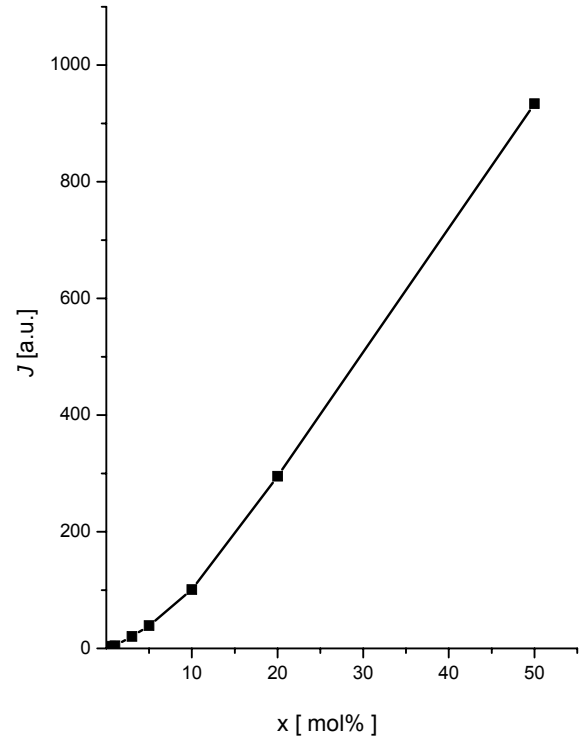
Fig. 1. EPR absorption spectra due to Mn^{2+} ions in $xMnO\cdot(100-x)[3B_2O_3\cdot BaO]$ glasses for (a) $x \leq 5$ mol% and (b) $10 \leq x \leq 50$ mol%.

The absorption line at $g_{eff} \approx 2.0$ is prevalent in the spectrum for $0.5 \leq x \leq 50$ mol%. For $x \leq 5$ mol %, this line shows hyperfine structure (hfs) characteristic to the ^{55}Mn (I=5/2) isotope. The resolution depends on the MnO concentration as it can be seen in figure 1(a). The resolution of the line is loosing with the increasing of the concentration due to the dipolar interactions in the manganese ion surrounding [24-26].

The hyperfine sextet is due to isolated Mn^{2+} ions in high symmetric octahedral sites. The g factor and hyperfine coupling constant values ($A \approx 93$ G) and the well resolved hfs, show the predominantly ionic character of the bounding between Mn^{2+} and O^{2-} ions generating the octahedral symmetric ligand field. There are weak axial distortions superimposed on this field varying in intensity and orientation from a vicinity to another of the manganese ions [27, 28]. The hyperfine coupling constant, A, was approximated as separation between the lines of the central pair of the hfs sextet. For the sample having 0.5 mol% MnO this parameter was estimated as $A \approx 93$ G. Data available on the EPR of Mn^{2+} ions in glasses show that g and A parameters are not as sensitive to variation of local environment of these ions as the crystal field parameters D or E [29,30]. Computer simulation of EPR spectra for various borate glasses [31] explains the additional splitting of the $g_{eff} \approx 2.0$ hyperfine sextet as due to large distribution of D and E, the fine structure parameters.

For $x \geq 10$ mol% the EPR resonance line centered at $g_{eff} \approx 2.0$ does not have hfs, Fig. 1(b).

The concentration dependence of the intensity, J, obtained as an integral of the area under the corresponding EPR signals and the line width, ΔB, for the line at $g_{eff} \approx 2.0$ are presented in Fig. 2. For $x \leq 5$ mol % the intensity of the resonance line increases very slowly. The increasing of intensity is more pronounced for $x > 5$ mol% (Fig. 2(a)). The line width from $g_{eff} \approx 2.0$ is increasing almost linear until $x \leq 10$ mol % which suggests that the Mn^{2+} ions are involved in dipolar interaction responsible for the EPR line broadening. The dipolar interactions result in a large background line that is the envelope of all concentrations at $g_{eff} \approx 2.0$. This large line is superimposed on the hfs sextet. At higher concentration of MnO, the line width dependence on MnO content reduced its slope. These mean that for a higher content of manganese the dipolar broadening is balanced by narrowing mechanism due to superexchange type interaction between the manganese ions. The achieved doping level of the samples imposes the progressive clustering of manganese.



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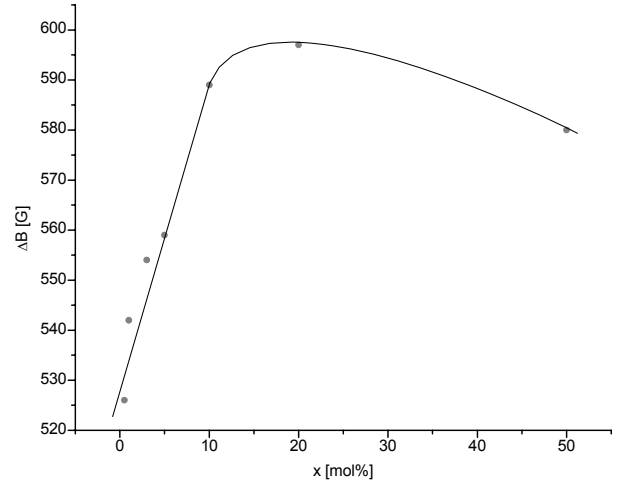
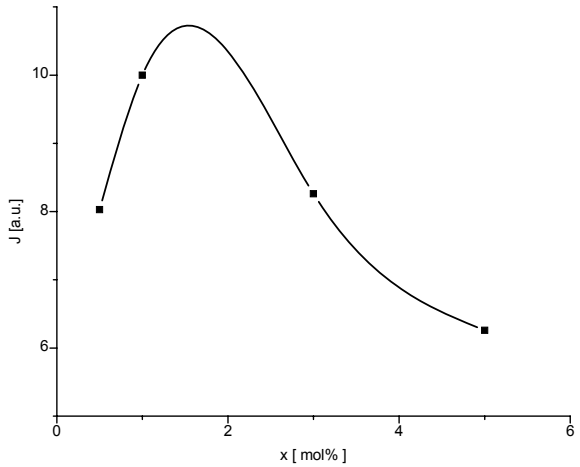


b

Fig. 2. Composition dependence of intensity (a) and the line-width (b) for the g ≈ 2.0 resonance absorption in the xMnO·(100-x)[3B_2O_3·BaO]glasses.

For 0.1 ≤ x ≤ 5 mol% MnO content the absorption line at g_{eff} ≈ 4.3 is present in the spectra and does not show hyperfine structure. Superimposed on this absorption line, the narrow line corresponding to accidental impurities of Fe^{3+} ions was also detected (Fig. 1(a)).



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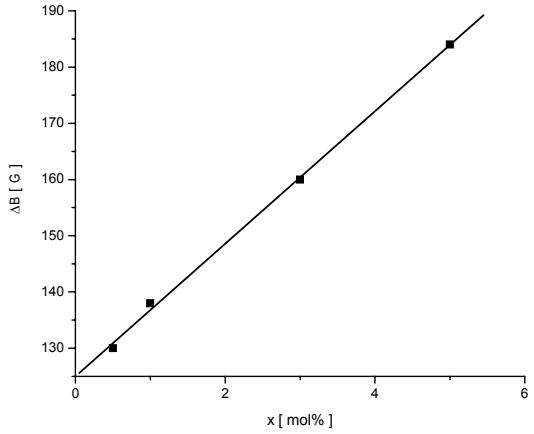

b

Fig. 3. Composition dependence of intensity (a) and the line-width (b) for the g ≈ 4.3 resonance absorption in the xMnO·(100-x)[3B_2O_3·BaO].

The concentration dependence of the intensity, *J*, and line width, ΔB, for the absorption near the g_{eff} ≈4.3 are presented in Fig. 3. The line intensity at g_{eff} ≈ 4.3 shows an increase up to 1 mol% MnO, followed by an abrupt decrease (Fig. 3(a)). The Mn^{2+} ions involved in this resonance absorption are isolated and therefore the line-width, generally, it cannot be correlated with the increase of manganese ion content. The lack of hfs at g_{eff} ≈4.3 absorption line is due to fluctuation of the ligand field parameters in the Mn^{2+} ion vicinity and the random distribution of the octahedral distortions vicinity [19]. Some of the low-symmetry centers no longer contribute to the isotropic absorption and the resulting EPR line is broadened due to anisotropy and the distribution of ligand field parameters.

The structure of our glasses show an evolution depending of MnO content from structural units involving Mn^{2+} ions in well defined vicinities, to structural units containing clustered magnetic ions. The changes of the shape of EPR absorption and parameters at g_{eff} ≈4.3 and

$g_{eff} \approx 2.0$ lines when the content of manganese ions are increasing revealed this evolution. The line intensity at $g_{eff} \approx 4.3$ is small enough to indicate a relative low concentration of Mn^{2+} ions involved in such structural units.

4. Conclusions

Glasses of the $xMnO\cdot(100-x)[3B_2O_3\cdot BaO]$ system were obtained up to 50 mol% MnO.

The EPR investigation of Mn^{2+} ions on different types of structural units depends on the MnO content. In the low concentration range, the isolated Mn^{2+} ions were identified in sites of slightly tetragonally distorted octahedral symmetry. They give rise to absorptions at $g_{eff} \approx 2.0$ having a resolved hfs up to 5 mol % MnO. Isolated Mn^{2+} ions in sites of heavily distorted octahedral symmetry with strong crystalline field give resonance line at $g_{eff} \approx 4.3$. The intensity of this line is small enough to indicate a relative low concentration of Mn^{2+} ions involved in such structural units.

For $x \geq 10$ mol%, the progressive clustering of manganese ions was evidenced by the evolution of the $g_{eff} \approx 2.0$ absorption line.

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